

Table of contents

Abstract	VII
Kurzzusammenfassung	VIII
1 Introduction.....	1
1.1 Supramolecular modulation towards dynamic materials	1
1.2 Molecular photoswitches and motors.....	4
1.3 Spiropyrans for chiroptical switches	7
1.4 Dithienylethenes towards autoamplification.....	8
1.5 Emerging photoswitches and molecular motors.....	10
1.6 Photomodulation of vesicles.....	11
1.7 Photochromic supramolecular assemblies.....	11
1.8 Photoresponsive supramolecular gels.....	15
1.9 Photomodulation of oligonucleotides by non-covalent interactions	17
1.10 Cell penetration and photochromic peptides.....	21
2 Aim of the project.....	25
3 Results and Discussion	27
3.1 Photoresponsive self-healing supramolecular hydrogel.....	28
3.1.1 Synthesis and photoisomerization of the supramolecular gelator 1	28
3.1.2 Properties of supramolecular hydrogel 1	29
3.1.3 Supramolecular hydrogels dissipating with light	34
3.1.4 Drug release from hydrogels triggered by light.....	37
3.1.5 Hypothesis of supramolecular structure	39
3.2 Photocontrol of drug release from hydrogels with green light.....	42
3.2.1 Supramolecular gelator F ₂ -PAP-DKP-Lys	42
3.2.2 Supramolecular gelator F ₄ -PAP-DKP-Lys	53
3.3 Tetra- <i>ortho</i> -fluoroazobenzene as photochromic building blocks	60
3.3.1 Visible light activated catenanes as catalysts	60
3.3.2 Photochromic peptides.....	63
3.3.3 Photochromic building block for metal-organic framework	68
3.4 Supramolecular red-light-responsive supergelator.....	70

3.4.1	Synthesis of tetra- <i>ortho</i> -chloroazobenzene and Cl ₄ -PAP-DKP-Lys ₂	70
3.4.2	Photophysical properties Cl ₄ -PAP-DKP-Lys ₂	73
3.4.3	Supramolecular hydrogels dissipating with red light	73
3.4.4	Outlook Cl ₄ -PAP-DKP-Lys ₂	75
3.5	3-Arylazopyridinium derivatives switchable with green light	77
3.5.1	Synthesis of 3-arylazopyridinium salts	81
3.5.2	Physical properties of Z-isomers of selected 3-arylazopyridinium salts	82
3.5.3	Photo-oxidation of compounds 62 and 63	84
3.5.4	Comparison of 3-arylazopyridinium salts and azobenzene in oligopeptides	86
4	Conclusion and outlook	89
4.1	Photoresponsive self-healing supramolecular hydrogels	89
4.1.1	Outlook F ₄ -PAP-DKP-Lys 3	91
4.1.2	Supramolecular red-light-responsive supergelator Cl ₄ -PAP-DKP-Lys ₂	92
4.1.3	Outlook Cl ₄ -PAP-DKP-Lys ₂	92
4.1.4	Tetra- <i>ortho</i> -fluoroazobenzene and 3-arylazopyridinium as photochromic building blocks	92
5	Experimental part	95
5.1	Laboratory standards	95
5.1.1	Solvents and reagents	95
5.1.2	Nuclear magnetic resonance spectroscopy (NMR)	95
5.1.3	UV-Vis spectrophotometer	96
5.1.4	Rheometry	96
5.1.5	High-power ultrasonic cleaning unit	97
5.1.6	Infrared spectroscopy (IR)	97
5.1.7	Analytic and preparative HPLC	97
5.1.8	Lyophilization	97
5.1.9	Mass spectrometry (EI, FAB, GC-MS and ESI)	97

5.1.10 Elemental analysis (EA)	98
5.1.11 Thin layer chromatography (TLC)	98
5.1.12 Analytical balance.....	98
5.1.13 TEM and SEM microscope	98
5.1.14 Preparative work	99
5.1.15 Product purification	99
5.1.16 LED and isomerization	100
5.2 PAP-DKP-Lys	101
5.2.1 Synthesis of PAP-DKP-Lys.....	101
5.2.2 Photophysical properties PAP-DKP-Lys.....	104
5.2.3 Gelation properties of PAP-DKP-Lys	106
5.3 F ₂ -PAP-DKP-Lys	119
5.3.1 Synthesis of F ₂ -PAP-DKP-Lys.....	119
5.3.2 Photophysical properties of the gelator F ₂ -PAP-DKP-Lys 2	127
5.3.3 Gelation properties of F ₂ -PAP-DKP-Lys	134
5.3.4 Guest release from hydrogels using green light	144
5.4 F ₄ -PAP-DKP-Lys	166
5.4.1 Synthesis of F ₄ -PAP-DKP-Lys.....	166
5.4.2 Photophysical properties of F ₄ -PAP-DKP-Lys	178
5.4.3 Gelation properties of F ₄ -PAP-DKP-Lys	182
5.5 Synthesis of tetra- <i>ortho</i> -fluoro-azobenzenes.....	191
5.5.1 Synthesis of <i>ortho</i> -F ₄ -4,4'-bis(hydroxymethyl)azobenzene.....	195
5.5.2 (<i>E</i>)-4-(4-Tetra- <i>ortho</i> -F ₄ -azobenzamido)naphthalene-2,6-dicarboxylate.....	199
5.5.3 (<i>E</i>)- <i>ortho</i> -F ₄ -4-(N-Fmoc-aminomethylphenylazo)benzoic acid....	204
5.5.4 (<i>E</i>)-Phenyl- <i>ortho</i> -F ₄ - <i>para</i> -azobenzoic acid	208
5.6 Cl ₄ -PAP-DKP-Lys ₂	213
5.6.1 (<i>S</i>)-Boc-Phe(3,5-Cl ₂ -4-NH ₂)-OMe	213
5.6.2 Synthesis of Cl ₄ -PAP-DKP-Lys ₂	218
5.6.3 Photophysical properties Cl ₄ -PAP-DKP-Lys ₂	228

5.6.4	Gelation properties of Cl ₄ -PAP-DKP-Lys ₂	231
5.7	Phenylalanine-containing cyclic dipeptides	235
5.8	Photochromic tyrosine based on spiropyrans.....	241
5.9	3-Arylazopyridinium derivatives	245
5.9.1	Solid-phase synthesis 3-arylazopyridinium derivatives	269
5.9.2	Photophysical properties of 3-arylazopyridinium derivatives.....	274
5.10	Dicarboxylic acid linker.....	283
5.11	[4,4'-Bipyridine]-3,5-dicarbonitrile	287
6	Abbreviation	291
6.1	Abbreviation index	291
7	Literature	293
7.1	Literature index	293
8	Appendix	IX
8.1	Curriculum Vitae.....	IX
9	Acknowledgements	XII